MAGNETIZABLE DEVICE

This invention relates to a magnetizable device which comprises a magnetic layer composed of domain-separated, nanoscale (e.g. 1-100nm) ferromagnetic
5 particles. The magnetizable device of the invention may be used as a magnetic storage device having improved data storage characteristics. In particular, the invention relates to magnetic storage media comprising single-domain, domain-separated, uniform,
10 ferromagnetic nanoscale (e.g. 1-100 nm) particles which may be arranged into a regular 2-D packed array useful in the storage of information.

Among the possible pathways to ultrahigh-density ($>=1$ Gbit/in^2) magnetic media is the use of nanoscale
15 (1-100 nm) particles. Beyond the standard requirements for magnetic media, a viable particulate media should have a small standard deviation in particle size as well as the particles being exchange decoupled. These requirements are necessary to avoid adverse media
20 noise. Current methods of fabricating nanoscale particles, such as arc-discharge or multiple target ion-beam sputtering, have not fully addressed these two requirements. Moreover, if the uniform particles are arranged into an ordered array, each particle can
25 represent a "bit" of information at a predictable location further increasing the media's efficiency. This invention details methods of producing particulate media that meet these requirements for ultrahigh-density recording. This invention is also an open
30 system which allows for the production of a variety of magnetic materials, such that the media can be tuned for different applications.

In particular this invention details the use of an iron storage protein, ferritin, whose internal cavity
35 is used to produce the nanoscale particles. Ferritin is utilised in iron metabolism throughout living

-2-

species and its structure is highly conserved among them. It consists of 24 subunits which are arranged to provide a hollow shell roughly 8 nm in diameter. The cavity normally stores 4500 iron(III) atoms in the form

5   of paramagnetic ferrihydrite. However, this ferrihydrite can be removed (a ferritin devoid of ferrihydrite is termed "apoferritin") and other materials may be incorporated. Examples include ceramics, superparamagnetic magnetite, acetaminophen,

10 and even the sweetener aspartame. To address magnetic media concerns, the invention incorporates ferromagnetically ordered materials.

According to a first aspect of the present invention, there is provided a magnetizable device

15 which comprises a magnetic layer composed of domain-separated, ferromagnetic particles each of which has a largest dimension no greater than 100nm.

According to a second aspect of the invention, there is provided a magnetic recording medium which

20 includes a magnetizable layer, wherein said magnetizable layer comprises a plurality of ferromagnetic particles each having a largest dimension no greater than 100nm, and each of which particles represents a separate ferromagnetic domain. The

25 magnetizable layer is preferably supported on a non-magnetic substrate.

According to a third aspect of the present invention, there is provided a magnetic composition comprising a plurality of ferromagnetic particles each

30 of which is bound to an organic macromolecule, and each of which has a largest dimension no greater than 100nm. In this aspect of the invention, it is preferred that said organic macromolecule is ferritin from which the normal core ferrihydrite has been removed and replaced

35 by a ferromagnetic particle.

As used herein, the term "ferromagnetic" embraces

materials which are either "ferromagnetic" and
"ferrimagnetic". Such usage is common in the
electrical engineering art.

The ferromagnetic particles used in the invention
5   should be of a material and size such that they possess
ferromagnetic properties at ambient temperatures (e.g.
15°C to 30°C),

Preferably, the ferromagnetic particles each have
a largest dimension no greater than 50nm, more
10 preferably less than 25nm and most preferably smaller
than 15nm. The largest dimension of the ferromagnetic
particles should not be so small that the particle will
lose its ferromagnetic property and become
superparamagnetic at the desired operating temperature
15 of the recording medium. Typically, for operation at
ambient temperature, this means that the magnetic
particles will normally be no smaller than about 3nm in
their largest diameter.

In the magnetizable device of the first aspect of
20 this invention and the magnetic recording medium of the
second aspect of this invention, the distance between
adjacent ferromagnetic domains is preferably as small
as possible to permit the maximum number of discrete
domains in a given area, and provide the maximum
25 storage capacity for the recording medium. The actual
lower limit will vary for different materials and other
conditions such as the temperature at which the
recording medium is to be used. The key requirement,
however, is that neighbouring domains should not be
30 able to interfere magnetically with each other to the
extent that the magnetic alignment of any domain can be
altered by neighbouring domains. Typically, the lower
limit on the spacing of the domains is about 2nm. The
distance between adjacent domains will be determined by
35 the density of discrete domains required. Typically,
however, to take advantage of the miniaturization

possibilities provided by the invention, the distance
between adjacent domains will be no greater than 10nm.

Generally the particles will be uniform in size,
by which we mean that the particles do not vary in
5   largest diameter by more than about 5%. One of the
advantages of the use in the invention of an organic
macromolecule which binds a magnetic particle by
surrounding it is that this can be used to select
particles of a uniform size.

10   In the case where the particles are spheroidal, it
will be the diameter of the particles which must be no
greater than 100nm.

In preferred embodiments of all aspects of this
invention, each ferromagnetic particle is encased, or
15   partially encased, within an organic macromolecule.
The term macromolecule means a molecule, or assembly of
molecules, and may have a molecular weight of up
1500kD, typically less than 500kD. Ferritin has a
molecular weight of 400kD.

20   The macromolecule should be capable of binding by
encasing or otherwise organising the magnetic particle,
and may therefore comprise a suitable cavity capable of
containing the particle; a cavity will normally be
fully enclosed within the macromolecule.

25   Alternatively, the macromolecule may include a suitable
opening which is not fully surrounded, but which
nevertheless is capable of receiving and supporting the
magnetic particle; for example, the opening may be that
defined by an annulus in the macromolecule. For

30   example, suitable macromolecules which may be used in
the invention are proteins, for example the protein
apoferritin (which is ferritin in which the cavity is
empty), flagellar L-P rings, cyclodextrins, self-
assembled cyclic peptides. As an alternative to

35   encasing the magnetic particles within the
macromolecule, they may be organised on the

macromolecule, such as on a bacterial S-layer.

Other materials which may be used in the invention to organise the ferromagnetic particles are inorganic-silica networks such as MCM type materials, dendrimers

5 and micellar type systems.

The presently preferred macromolecule for use in the invention is the apoferritin protein which has a cavity of the order of 8nm in diameter. The ferri- or ferromagnetic particles to be accommodated within this

10 protein should have a diameter no greater than 8nm.

The bound particles of this aspect of the present invention with a coating that inhibits aggregation and oxidation, also helping them to be domain-separated.

In the magnetizable device of the first aspect of

15 this invention and the magnetic recording medium of the second aspect of this invention, the particles are preferably arranged in a 2-D ordered array which would yield an ultrahigh-density magnetic media.

The ferromagnetic material may be a metal, such as

20 cobalt, iron, or nickel; a metal alloy, such as an alloy which contains aluminium, barium, bismuth, cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, praseodymium, samarium, strontium, titanium, vanadium,

25 ytterbium, yttrium or a mixture thereof; a metal ferrite such as a ferrite containing barium, cobalt, or strontium; or an organic ferromagnetic material.

When generating nanoscale particles, one major concern is that the particles produced are not

30 superparamagnetic. Superparamagnetic particles are those which have permanent magnetic dipole moments, but the moments' orientations with respect to the crystallographic axes fluctuate with time. This is not useful for a practical magnetic storage media.

35 Superparamagnetism depends on the volume, temperature, and anisotropy of the particles. Via energy

considerations, one can derive an equation relating
these quantities. The volume at which a particle
becomes superparamagnetic (V_p) is given by: $V_p =$
$25kT/K$, where k is Boltzman's constant, T the

5   temperature of the particle in degrees Kelvin, and K
the anisotropy constant of the material. Using this
formula, it is possible to determine the temperature at
which a particle becomes superparamagnetic (the
"blocking temperature") for a given material at a fixed

10 volume. In our specific case, the fixed volume is 8 nm
in ferritin. If a cobalt metal particle with only
crystalline anisotropy (that value being 45×10^5) is a
sphere with a diameter of 8 nm, the blocking
temperature is 353 °K. This is within the range of

15 temperatures experienced within a hard disk drive, and
the cobalt particles may prove to be a useful storage
medium. Obviously, there are other considerations such
as the materials' coercivity, moment, saturation
magnetisation, and relaxation time. By tuning the

20 materials incorporated into the ferritin, though, these
can be addressed.

    Ferritin is utilised in iron metabolism throughout
living species and its structure is highly conserved
among them. It consists of 24 subunits arranged in a

25 432 symmetry which provide a hollow shell roughly 8 nm
in diameter. The cavity normally stores 4500 iron(III)
atoms in the form of paramagnetic ferrihydrite.
However, this ferrihydrite can be removed (a ferritin
devoid of ferrihydrite is termed "apoferritin") and

30 other materials may be incorporated. The subunits in
ferritin pack tightly, however there are channels into
the cavity at the 3-fold and 4-fold axes. Lining the
3-fold channels are residues which bind metals such as
cadmium, zinc, and calcium. By introducing such

35 divalent ions one can potentially bind ferritin
molecules together, or at least encourage their

proximal arrangement.

One method of preparing a 2-D packed array of
ferromagnetically ordered particles of uniform size up
to 8 nm includes the removal of the ferrihydrite core
5   from the native ferritin in aqueous solution, the
incorporation of ferromagnetically ordered cobalt metal
particles by sodium borohydride reduction of the
aqueous Co(II) solution into the ferritin cavities, the
generation of a narrow size distribution through
10   ultracentrifugation, the injection of particles into an
MES/glucose subphase solution upon which the 2-D array
assembles, and the transfer of the 2-D array to a
substrate which is then carbon coated. In this method,
the ferritin source may be a vertebrate, invertebrate,
15   plant, fungi, yeast, bacteria, or one produced through
recombinant techniques.

In the method described, a metal alloy core may be
produced by sodium borohydride reduction of a water
soluble metal salt. Other oxidation methods include
20   carbon, carbon monoxide, hydrogen, or hydrazine hydrate
solution. Alternatively, a suitable solution may be
oxidised to yield a metal ferrite core. Oxidation may
be chemical or electrochemical to yield the metal
ferrite.

25   In this method, other methods of selecting a
narrow size distribution may be employed such as short
or long column meniscus depletion methods or magnetic
field separation.

Further, in this method, divalent metal salts
30   containing cadmium, calcium, or zinc may be added into
the subphase solution to aid in particle ordering.

Further, in this, other methods of arranging the
particles into a 2-D array may be employed, such as
solution evaporation onto a solid substrate.

35   Further, in this method, the 2-D array may be
coated with carbon-based films such as hydrogenated or

nitrogen doped diamond-like carbon, or with silicon-
based films such as silicon dioxide.

In the present invention, ferritin may be used to
enclose a ferromagnetic particle whose largest
dimension is limited by ferritin's inner diameter of 8
nm. The particles are produced first by removing the
ferrihydrite core to yield apoferritin. The is done by
dialysis against a buffered sodium acetate solution
under a nitrogen flow. Reductive chelation using
thioglycolic acid is used to remove the ferrihydrite
core. This is followed by repeated dialysis against a
sodium chloride solution to completely remove the
reduced ferrihydrite core from solution. Once the
apoferritin is produced, ferri- or ferromagnetic
particles are incorporated in the following ways. The
first is by reducing a metal salt solution in the
presence of apoferritin. This is performed in an inert
atmosphere to protect the metal particles from
oxidation which would lessen their magnetic benefit. A
combination of metal salts in solution can also be
reduced to generate alloys or alloy precursors.
Sintering or annealing in a magnetic field may be
necessary to generate the useful magnetic alloys.
Another method is to oxidise a combination of an
iron(II) salt and another metal salt. This gives a
metal ferrite particle which does not suffer negatively
from oxidation. The metal salts which are beneficial
include salts of aluminium, barium, bismuth, cerium,
chromium, cobalt, copper, iron, manganese, molybdenum,
neodymium, nickel, niobium, platinum, praseodymium,
samarium, strontium, titanium, vanadium, ytterbium, and
yttrium.

A narrow size distribution of particles is
necessary to avoid media noise. Such a distribution
can be obtained through a variety of procedures
including, but not limited to, density gradient

centrifugation or magnetic field separation.

While the production procedure detailed uses native horse spleen ferritin, this invention should not be seen as limited to that source. Ferritin can be

5 found in vertebrates, invertebrates, plants, fungi, yeasts, bacteria, or even produced through recombinant techniques. By creating mutant apoferritins lacking the divalent binding site, others have found that the mutant proteins assemble into oblique assemblies as

10 opposed to the regular hexagonal close-packed.

While ferritin seems to be an ideal system for generating nanoscale particles, it is not the only system available. For example, flagellar L-P rings are tubular proteins with an inner diameter of 13 nm. By

15 creating a 2-D array of these proteins, metal films could be deposited into the tubular centres to create perpendicular rods of magnetic material. Also metal reduction in the presence of a microemulsion can be used to generate nanoscale particles which are coated

20 with surfactant. This invention is open to other nanoscale particle production methods.

Finally an ordered arrangement of the particles is desired. One way to accomplish this is by injecting an aqueous solution of particles into an MES/glucose

25 subphase solution contained in a Teflon trough. The particles spread at the air-subphase interface, and a portion denature to form a monolayer film. The 2-D arrangement of encased particles occurs underneath this monolayer. After 10 minutes at room temperature, the

30 arrangement and monolayer are transferred to a substrate by placing the substrate directly onto the monolayer for 5 minutes. After withdrawing the substrate, the attached arrangement is coated with a thin layer of carbon for protection. Other methods

35 such as solution evaporation onto a solid substrate can also give 2-D arrangements, and this invention should

-10-

not be seen as limited in its arrangement methods.

EXAMPLE 1

This example illustrates the preparation of
apoferritin from horse spleen ferritin. Apoferritin

5   was prepared from cadmium-free native horse spleen
ferritin (CalBiochem, 100 mg/ml) by dialysis (molecular
weight cut-off of 10-14 kDaltons) against sodium
acetate solution (0.2 M) buffered at pH 5.5 under a
nitrogen flow with reductive chelation using

10   thioglycolic acid (0.3 M) to remove the ferrihydrite
core. This is followed by repeated dialysis against
sodium chloride solution (0.15 M) to completely remove
the reduced ferrihydrite core from solution.

EXAMPLE 2

15   This example illustrates the preparation of cobalt
metal within apoferritin. The apoprotein is added to a
deaerated TES/sodium chloride solution (0.1/0.4 M)
buffered at pH 7.5 to give an approximate 1 mg/ml
working solution of the protein. A deaerated

20   cobalt(II) [for example, as the acetate salt] solution
(1 mg/ml) was added incrementally such that the total
number of atoms added was approximately 500
atoms/apoprotein molecule. This was allowed to stir at
room temperature for one day in an inert atmosphere.

25   This is followed by reduction of the cobalt(II) salt
with sodium borohydride to cobalt(0) metal. The final
product yielded a solution of cobalt particles, each
surrounded by a ferritin shell.

EXAMPLE 3

30   This example illustrates the preparation of a
metal alloy such as yttrium cobalt (YCo_5) within
apoferritin. The metal alloy follows the same procedure
as Example 2 but using a 1:5 ratio of yttrium(III) [for
example, as the acetate salt] to cobalt(II) [for

35   example, as the acetate salt]. The final product
yielded a solution of yttrium cobalt particles, each

-11-

surrounded by a ferritin shell.

EXAMPLE 4

This example illustrates the preparation of a metal ferrite such as cobalt ferrite ($CoO \cdot Fe_2O_3$) within

5   apoferritin. The apoprotein is added to a deaerated MES/sodium chloride solution (0.1/0.4 M) buffered at pH 6 to give an approximate 1 mg/ml working solution of the protein. A deaerated solution of cobalt(II) [for example, as the acetate salt] and iron(II) [for

10   example, as the ammonium sulphate salt] in a ratio of 1:2 is added incrementally and allowed to air-oxidise. The final product yielded a solution of cobalt ferrite particles, each surrounded by a ferritin shell.

EXAMPLE 5

15   This example illustrates the 2-D arrangement of ferritin-encased magnetic particles. An aqueous solution of particles [from Examples 2-4, and whose uniformity in size has been selected] is injected into an MES/glucose subphase solution (0.01 M/2%) contained

20   in a Teflon trough. The particles spread at the air-subphase interface, and a portion denature to form a monolayer film. The 2-D arrangement of encased particles occurs underneath this monolayer. After 10 minutes at room temperature, the arrangement and

25   monolayer are transferred to a substrate by placing the substrate directly onto the monolayer for 5 minutes. After withdrawing the substrate, the attached arrangement is coated with a thin layer of carbon for protection.